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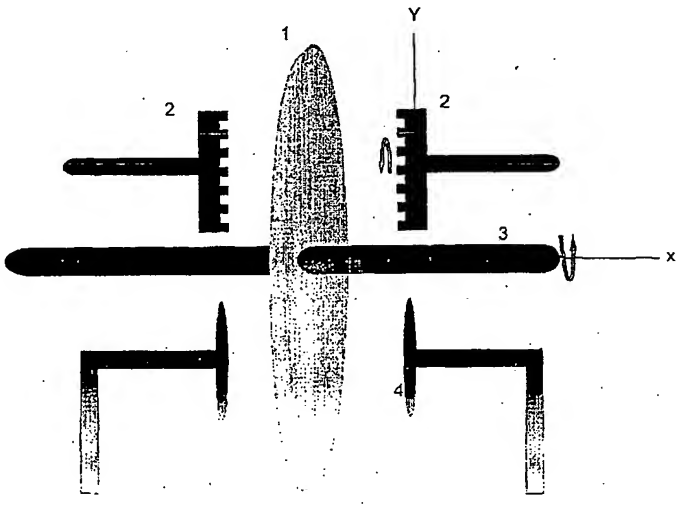

An ink-jet printing device wherein the substrate is arranged in a vertical position.

(57) Abstract: A method of forming a magnetic recording device having a film of magnetisable nanoparticles, which comprises preparing a suspension of magnetisable nanoparticles in a carrier fluid and depositing said fluid suspension onto a substrate surface as droplets having a volume less than about 1 nl to form said film of magnetisable nanoparticles as a dry residue of the deposited fluid suspension. The invention also broadly relates to methods of forming magnetisable, inorganic and protein films.

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PRODUCTION OF NANOPARTICULATE THIN FILMS

Introduction

[0001] The present invention relates to the production of thin films by ink jet printing. The films obtained may be used in a number of applications, for example as components in magnetic media and semiconductive media.

Background of the Invention

[0002] A broad variety of methods are available for the fabrication of thin films, for example, chemical vapour deposition, molecular-beam epitaxy, evaporation, sputtering and spin coating (*"Handbook of Thin Film Materials: Vol. 1 Deposition and processing of thin films" 2002 Ed. Nalwa H. S., Academic Press; "Thin Films on Glass" 1997 Eds. Bach Kraus, Springer-Verlag*) . Sputtering and electro-evaporation have traditionally been the preferred methods of choice for the production of magnetic media for disk drives in the computer industry.

[0003] The fabrication of self-assembled protein arrays has attracted considerable interest because such arrays offer a variety of applications in contemporary nanotechnology, for example as semiconductor devices and biosensors (*Yun S C et.al. 2001, MRS Symposium Proc. j2.3/1-j2/3/6; McMillan A et.al. 2002 NatureMaterials 1 (4) 247-252*). The processes for creating protein thin films have focussed largely on the formation of films by a two stage process. Firstly, 2-D protein arrays are formed on a liquid film. These films are then transferred to a solid substrate such as a silicon wafer. The Langmuir-Blodgett technique (*Britt D W et.al. Phys. Chem. Chem. Phys. 2000 2 4594-4599*) is a well-known film fabrication technique which involves the formation of protein arrays at a lipid-air interface. Several other methodologies on this basic theme have also been described, for example the formation of self-assembled protein arrays at an air-water interface (*Kobayashi K et.al. 2001 Biosci. Biotechnol. Biochem. 65 (1) 176-179*), a mercury-air interface and liquid-gas interface (*Nagayama K et.al. 1995 Jpn J Appl. Phys. 34 pages 3947-3954*) and a gallium-aqueous interface (*Adachi E et.al. 1998 Chem. Phys. Lett. 284 440-445*). Protein thin-films have also been created by spray coating and vapour deposition (*Goodall S et.al. 2002 J. Aerosol Med.15 (3) pages 351-357*).

[0004] In the diagnostics industry, the deposition of discrete units of a particular protein on solid substrates by ink-jet printing has been described (*Roda A et.al. 2000 Biotechniques 28 (3) pages 492-496*; WO96/22533). Here, the objective is to obtain an array of immobilised individual proteins which can be used to screen for unitary targets. Ink-jet printing is the conventional technology for printing computer-derived information onto paper (*Calvert P 2001 Chem. Mater. 13 3299-3305*). Whilst unitary dots may be applicable to some applications, other applications such as magnetic recording demand very smooth and continuous films.

[0005] We have now found, surprisingly, that ink-jet printing represents an effective technique for the formation of thin films of proteins, magnetic particles and also magnetic particles and semiconductor nanoparticles which are encapsulated, at least partially, by a macromolecular material.

Summary of the Invention

[0006] **In a first aspect of the invention** there is provided a method of forming a magnetic recording device having a film of magnetisable nanoparticles, which comprises preparing a suspension of magnetisable nanoparticles in a carrier fluid and depositing the said fluid suspension onto a substrate surface as droplets having a volume less than about 1nl to form said film of magnetisable nanoparticles as a dry residue of the deposited fluid suspension.

[0007] **In a second aspect of the invention**, there is provided a method of forming a magnetisable film, which comprises preparing a suspension of magnetisable nanoparticles, each having been formed at least partially within a protein shell, in a carrier fluid and depositing the said fluid suspension onto a substrate surface as droplets having a volume less than about 1nl to obtain said magnetisable film on the substrate as a dry residue of the deposited fluid suspension.

[0008] **In a third aspect of the invention**, there is provided a method of forming a film of inorganic nanoparticles on a substrate, which comprises preparing a suspension of inorganic nanoparticles, each having been formed at least partially within a protein shell, in a carrier fluid and depositing the said fluid suspension onto a substrate surface as

droplets having a volume less than about 1nl to obtain said film on the substrate as a dry residue of the deposited fluid suspension.

[0009] **In a fourth aspect of the invention** there is provided a method of forming a protein thin film on the surface of a substrate, said protein thin film having a thickness of less than about 10 times the diameter of its constituent protein particles substantially throughout the film, which comprises preparing a suspension of protein particles in a carrier fluid, said protein particles having been subjected to a membrane filtration step, and depositing the said fluid suspension onto a substrate surface as droplets having a volume less than about 1nl to obtain said film on the substrate as a dry residue of the deposited fluid suspension.

[0010] **In a fifth aspect of the invention** there is provided a magnetic recording device having a film of magnetisable nanoparticles, wherein said particles have been prepared in a suspension in a carrier fluid and deposited onto a substrate surface as droplets having a volume less than about 1 nl to form said film of magnetisable nanoparticles as a dry residue of the deposited fluid suspension.

Brief Description of the Drawings

For further illustration of the present invention, and without limitation, embodiments will now be described with reference to the accompanying drawings. In the drawings:

Fig. 1. An ink-jet printing device wherein the substrate is arranged in a vertical position.

Fig. 2. A substrate positioning device in a first substrate-disengaged position and second substrate-engaged position.

Fig. 3. An ink-jet printing device wherein the spindle is in a retracted position.

Fig. 4. An ink-jet printing device wherein a substrate is arranged in a horizontal position.

Fig. 5. A tapping-mode AFM image of ferritin deposited onto a glass substrate.

Fig. 6. *A tapping-mode AFM image of ferritin deposited onto (a) a non-irradiated glass substrate and (b) a glass substrate which has been irradiated with UV light.*

Detailed Description of the Invention

[0011] The process of ink jet printing involves the deposition of small, typically sub-nanolitre, quantities of liquid material through a plurality of micro-nozzles onto a substrate. Typically, the deposition process will involve either piezoelectric or thermally-assisted operation of the printing nozzles. The quantity of liquid deposited per droplet will generally be greater than about 0.1 picolitres, for example greater than about 1 picolitre. This quantity may be less than about 1 nanolitre, for example less than about 100 picolitres or less than about 10 picolitres. In a preferred aspect of the invention, the quantity of liquid deposited per droplet is about 3 picolitres.

[0012] Nozzle-deposition of picolitre amounts of material enables fine control of the volume of material deposited on a given area of substrate. Immediately prior to contact with a substrate the droplets may have a mass equal to that on exiting the ink jet nozzle. Alternatively, the individual droplets may subdivide into a finer "spray" of sub-droplets before contacting the substrate. Where the droplets form such a spray, its characteristics will largely be determined by the size of starting droplet and the distance of the nozzle head from the substrate. The extent to which the droplets subdivide will, in turn, determine the area of substrate covered. The fine apertures provided by ink-jet printing permit a high degree of control in respect of ink-jet derived nanoparticulate droplets.

[0013] Further, ink-jet printing technologies may be conveniently incorporated into industrial manufacturing processes and are likely to require considerably less raw material in terms of weight of coating material per unit area of substrate than would be the case in tank-based coating systems.

[0014] Where the particles are magnetic nanoparticles, they may be encapsulated, at least partially, within a macromolecular shell. Alternatively, the magnetic nanoparticles may be non-encapsulated. These particles may be formed by any means known to one skilled in the art, preferred methods yielding appropriate size and dispersity control. In an aspect of the invention, the magnetic nanoparticles are formed within a macromolecular shell

e.g. a protein. This shell may be subsequently removed, for example by laser pyrolysis, to leave a non-encapsulated magnetic nanoparticle. Magnetic nanoparticles may also be formed within surfactant micelles, which again may be subsequently removed, for example by dilution of the surfactant solution to a concentration below the cmc followed by filtration.

[0015] Where the particles are non-magnetic particles, for example semiconductor nanoparticles, they may be encapsulated, at least partially, by a protein shell. Alternatively, they may be formed within an encapsulating protein shell that is subsequently removed, for example by laser pyrolysis, to leave a non-encapsulated non-magnetic nanoparticle.

[0016] A magnetic recording medium is any medium having magnetic properties that make it capable of data storage. Preferably, but without limitation, the recording medium will be present in a hard-disk drive for example as used in computers, audio-equipment, vehicles, video-recorders etc. In addition, the medium may also be used in magnetic tape or magnetic card devices.

[0017] In some aspects of the invention, a magnetic recording device preferably has a data storage capacity of greater than 1 Gb / inch^2, preferably greater than 5 Gb / inch^2, more preferably greater than 10 Gb / inch^2 and most preferably greater than 20 Gbit / inch^2.

[0018] An ink-jet printer device for use in the present invention suitably comprises as main elements: (i) a reservoir for holding a suspension of the coating particles; (ii) an ink-jet head; (iii) a conduit connecting the reservoir to the ink-jet head; (v) a supporting element to maintain the substrate to be coated in a secure position; (vi) means for moving the ink jet head and the substrate relative to each other; (vii) a control means, for example computer software, for controlling the relative movement of the ink-jet head and the substrate. Optionally a valve may be included in the conduit line connecting the reservoir to the ink-jet head.

[0019] An ink-jet head, in turn, will usually suitably comprise (i) an inlet port; (ii) a reservoir portion for the coating particle suspension; (iii) a plurality of nozzles with apertures of a pre-determined size, preferably each nozzle comprising a smaller reservoir

portion; (iv) a mechanism for ejecting droplets of the coating suspension from the nozzles.

[0020] A variety of systems for ejecting ink-droplets are known, notably piezoelectric, thermal, electrostatic and acoustic methods (*Le H P 1998 J. Imaging Sci. Tech. 42 49-62).* For example in bubble-jet print heads each nozzle unit comprises a heating element. When the temperature of the element is raised momentarily to several hundred degrees a vapour bubble is created which displaces liquid ink forcing a droplet through the nozzle. In piezoelectric deposition, an electric field applied across a piezoelectric crystal located in the nozzle, usually a ceramic, causes the crystal to deform, thereby decreasing the volume of the nozzle available to the liquid and causing a droplet to be discharged from the orifice. Any of the above systems may be used in accordance with the present invention.

[0021] In the operation of an ink-jet application device suitable for the present invention, a suspension of particles is applied to a substrate via an ink-jet head. In a preferred embodiment the nozzles of the ink-jet head will be arranged substantially perpendicularly to the surface of the substrate. During the deposition process, the substrate and ink-jet head are moved relative to each other so that the ink-jet head can apply the particle suspension to the area of the substrate requiring coating. This relative movement may be accomplished by movement of the ink-jet head, the substrate or both. The distance between the surface of the substrate and the ink-jet nozzle may also be adjusted as required. Such adjustment will be within the ability of one of ordinary skill in this art.

[0022] The substrate is preferably circular but may be of any shape suitable for a given application.

[0023] In an aspect of the invention, the substrate surface is preferably as smooth as possible. The substrate surface does not have to be planar over its whole area but should be lacking substantial local discontinuities. In terms of surface roughness, the average surface roughness, R_a, is preferably less than about 1nm, for example about 0.1nm. Ra is determined by finding an average centreline running parallel to the surface. Any troughs below the centreline are inverted and counted as peaks. The average height of the peaks above the centreline, (inclusive of the inverted troughs), is the roughness average, R_a. The roughness average of the substrate surface may be measured using any technique

known to one skilled in the art for example, by profilometry, elipsometry or Atomic Force Microscopy or combinations thereof. For example, the Atomic Force Microscope may be used.

[0024] In an alternative aspect of the invention, the substrate has a greater degree of roughness. For example the average surface roughness, R_a, of the substrate is greater than about 1nm, preferably greater than about 5 nm. In this aspect, the surface roughness, R_a, is preferably less than about 30 nm, for example less than about 20 nm or about 10nm. It has been found that in some embodiments of the invention, greater adhesion between the substrate and the coating particles may be obtained by controlling the average size of the asperities.

[0025] The substrate also preferably has a high surface hardness, for example a Vickers hardness of greater than about 600 kg/mm, preferably greater than about 700 kg/mm. It is also desirable that the substrate has a high stiffness, for example with a modulus of elasticity greater than about 70 GPa, preferably greater than about 80 GPa and more preferably greater than about 90GPa. The substrate may also have a specific modulus of greater than about 25GPa, for example greater than about 30GPa or greater than about 35GPa. It is advantageous for the substrate to have a low coefficient of thermal expansion since this improves the readability of a recording device made from the coated substrate. The coefficient of thermal expansion is preferably less than 30 ppm K^{-1}, for example less than 20 ppm K^{-1}. In an especially preferred embodiment, the coefficient of thermal expansion of the substrate is less than 10 ppm K^{-1}. In preferred embodiments of the invention, the substrate has a low thermal conductivity. This raises the temperature at which the coated substrate may operate effectively as a magnetic recording device. Preferred substrates of the invention therefore have a thermal conductivity of less than 20 $Wm^{-1}K^{-1}$, for example less than 10 $Wm^{-1}K^{-1}$ or less than about 5 $Wm^{-1}K^{-1}$. Examples of suitable materials are glass for example TS-10SX as available from Ohara Inc Japan (15-30, Oyama 1-Chome, Sagamihara-Shi, Kanagawa, 229-1186 Tel : (81)42-772-2101, Fax : (81)42-774-1071, http://www.ohara-inc.co.jp) and aluminium. Where the material is aluminium it may be coated with Ni-phosphorous.

[0026] In one embodiment of the present invention the substrate is arranged vertically and the ink-jet head is arranged perpendicularly to said substrate (1) as shown in Figure 1.

At least one ink-jet head (2) is arranged perpendicularly to one side of the substrate. In another embodiment the device may comprise at least one ink-jet head arranged on either side of said substrate. The substrate is rotated about the spindle (3) about axis "X" whilst the arrangement of ink-jet head(s) remains stationary. Alternatively, the substrate may be held in a stationary position and the ink jet head(s) rotated about axis "X" or moved in a single plane "Y" substantially parallel to the surface of the substrate. In a preferred aspect of the invention, both the substrate and ink-jet undergo simultaneous movement. For instance, the substrate is rotated whilst the ink-jet head arrangement may either rotate about axis "X" or move in plane "Y". In embodiments where the substrate is rotated relative to the ink jet the angular velocity of rotation may be adjusted by the control means as a function of the radial position of the ink jet head in order to ensure that the area of substrate covered by the ink-jet head remains substantially constant. Typically the substrate will be disk-shaped.

[0027] Prior to coating, the substrate disk will be positioned on the spindle of an ink-jet application device for example as shown in Figs. 1 and 4. Fig. 2 shows a suitable positioning device comprising an arch-shaped structure (2) from which individual gripping members (3) project radially. In a first position (Fig. 2b) each member engages with the outer rim of the disk (1). Together, these members retain the disk within the arch-shaped structure and allow it to be accurately moved to a location for positioning onto the spindle. After the disk is positioned onto the spindle, the gripping members may be disengaged from the disk rim as shown in Fig 2a. The gripping members may for example be spring-formed structures or solid pins which are retractable along their longitudinal axis.

[0028] To load the disk into the ink-jet application device, the disk supporting spindle (3) may be retracted to a first position by a control device (4). The substrate disk may then be moved to the position within the application device as shown in Fig. 3. The disk is positioned into the application device such that the centre of the aperture of the disk is in line with the longitudinal axis of the retractable spindle. The retractable spindle may then be inserted through the central aperture of the disk. The disk is then clamped securely on the spindle. One skilled in the art will appreciate that disk clamping means such as washers and the like may be applied robotically to ensure that the disk is adequately fixed

in a plane perpendicular to the longitudinal axis of the spindle such that when the spindle is rotated with the desired velocity the disk will rotate and retain its position in a single plane. For example the spindle may have a cross-sectional area which can be enlarged such that it expands to fill the central aperture of the disk and secure it in a perpendicular position. One skilled in the art will also readily appreciate that a variety of devices may be used to rotate the spindle.

[0029] In another embodiment as shown in Fig. 4, the substrate may be held on a spindle in a substantially horizontal plane. An ink-jet head (1) is positioned over the substrate (2) and may move parallel to plane "X". In operation the substrate is rotated about the spindle (3) axis "X" whilst the arrangement of ink-jet head(s) remains stationary. Alternatively, the substrate may be held in a stationary position and the ink jet head(s) move in a plane "X" substantially parallel to the surface of the substrate. In a preferred aspect of the invention, both the substrate and ink-jet undergo simultaneous movement. For instance, the substrate is rotated whilst the ink-jet head arrangement may move in plane "X".

[0030] In operation one skilled in the art will appreciate that once the substrate is in a position for coating to be performed it will be securely engaged with the retaining means, for example the spindle. By "secure" we mean that the substrate will not deviate substantially from its position in a single plane such that ink-jet printing can be performed to the required degree of effectiveness without causing damage to either the ink-jet head or substrate.

[0031] In devices for use in the present invention one skilled in the art will appreciate that the dimensions of the ink-jet head may be selected according to a particular application. For example, an ink-jet head which is to be held in a stationary position, for example as described above for some embodiments of the device shown in Figures 1 and 4, may be designed such that its longitudinal dimension is substantially equal to the radius of the disk to which it is to be applied. Moreover, the number of nozzles used in a particular head will be determined by the surface area which is intended to be covered by the ink-jet head. One skilled in the art will appreciate that the number of nozzles and dimensions of the nozzles may be designed according to a particular application and that an ink-jet application device may be constructed to accommodate interchangeably different heads.

[0032] In a preferred embodiment of each aspect of the described inventions the substrate is treated to promote the dispersion of the applied suspension of particles thereon. Such treatment may comprise chemical, mechanical or radiation treatment or combinations thereof. For example, chemical treatment may involve the use of wetting agents such as alcohols, for example propan-1-ol, or the use of dispersants/surfactants such as NP40 (Accurate Chemical and Scientific, Westbury, NY 11590US, Tel: (516)333-2221 (800)645-6264, Fax: (516)997-4948). The dispersants may be applied to the substrate before the application of a suspension of particles. Alternatively, dispersants and/or wetting agents may be added to the suspension containing the particles to be formed as a film on the substrate. The quantity of wetting agent or dispersant required for optimal coating of the substrate will depend on the specific suspension but the quantity added should preferably not cause the surface tension at the nozzle orifice to be reduced to a value insufficient to maintain the suspension inside the nozzle in the absence of an additional ejecting force from within the ink jet head.

[0033] In some embodiments of the invention, the substrate surface is pretreated prior to coating. This may be carried out by for example, mechanical or radiation treatment. Mechanical treatment may comprise cleaning the substrate for example by chemical-mechanical polishing. Radiation treatment preferably includes exposure of the substrate to UV light.

[0034] The source of the pretreating agent will generally be positioned in the same plane as the ink-jet head (4). Typically the disk will be rotated in the direction shown (arrow) and the pre-treating agent, for example a radiation beam or chemical wetting agent, will contact the substrate before it is exposed to the ink-jet head. The duration of pre-treatment and the time interval between pre-treatment and coating will depend on the application. For example, both the source of the pre-treating agent and the ink-jet head may operate substantially simultaneously such that the pre-treatment comprises only one pass of the disk through the area targeted by the source of the pre-treating agent. In other embodiments an area of substrate may be subjected to several passes of the disk through the area targeted by the source of the pre-treatment agent. A time interval may then pass, before particles are deposited onto the substrate by ink-jet printing.

[0035] It is preferred to use a device as shown in Figure 1 which comprises ink-jet heads and a UV light source that are arranged in a plane substantially parallel to each other such that the ink-jet heads are arranged substantially perpendicularly to the substrate and the UV light source head (4) emits a beam in a plane that is also substantially perpendicular to the substrate.

[0036] The film may also be treated after deposition of the particles onto the substrate, for example by UV-curing, or exposure to IR light source or by heat. The film may also be annealed following deposition of the particles, for example by heating the substrate in a conventional annealing oven to a temperature of at least about 300 °C or by exposure to a laser beam. It is especially preferred to anneal films in cases where the film is intended for use as a component in a magnetic recording device, since this greatly improves the magnetic properties of the film.

[0037] In many aspects of the invention, for example magnetic nanoparticulate films for use in magnetic recording media, the surface of the film will preferably be as smooth and as planar as possible. The film surface does not have to be absolutely planar over its whole surface area but, due to the proximity of the reading head in operation, should be lacking substantial local discontinuities. For example, discontinuities in the film surface should preferably be less than about 13nm in height above the magnetic surface. This means that in the case of magnetic nanoparticles encapsulated within an apoferritin shell, the tolerance level for the size of discontinuities in the film surface is of the order of one particle diameter (including the encapsulating shell) for efficacy as a magnetic recording medium.

[0038] It is also preferred that the film thickness is no greater than 2 particle diameters (including any encapsulating shell) substantially throughout the film, especially in cases where the substrate is relatively smooth on the length scale of the coating particles.

[0039] In a preferred aspect of the invention, therefore, the film is substantially in the form of a continuous monolayer. The film should be substantially continuous in order to reduce the incidence of discontinuities in film thickness resulting from interfaces between areas of coated and uncoated substrate.

[0040] For example, we have been able to perform magnetic recording on a magnetizable device comprising ferritin-encapsulated magnetic nanoparticles on a substrate having an

average surface roughness R_a of less than about 1nm, where the variation in film thickness over the substrate is approximately 25nm (a single ferritin particle has a diameter of approximately half this value).

[0041] In other aspects of the invention, where the film is not used as a data storage medium, smoothness of the film surface may be less critical. The film smoothness required will depend on the specific application but in some aspects, for example, the average surface roughness of the film may not be greater than about 10, such as not greater than about 5 or not greater than about 3 or 2 particle diameters (including any encapsulating shell).

[0042] Since the substrate exhibits differing degrees of roughness in accordance with different aspects of the invention, the thickness of the film at a given point on the film surface will depend to some extent on the degree of surface roughness of the underlying substrate. In some aspects of the invention, therefore, the film thickness may not vary in depth by more than about 10 times the diameter of the constituent particles (including any encapsulating shell), more preferably not more than about 5 times the particle diameter and most preferably not more than about 3 or 2 times the particle diameter substantially throughout the film. The absolute film thickness will depend on the particle diameter but films made in accordance with the invention will usually have a thickness of less than about 500nm, more preferably less than about 100nm and most preferably less than about 50 nm. In especially preferred embodiments of the invention, the film thickness is less than about 30nm substantially throughout the film.

[0043] Where the present invention relates to a method for forming a magnetic recording device by depositing magnetic or magnetisable nanoparticles on a substrate as droplets having a volume less than about 1nl, for example by ink-jet printing, the magnetic particles may be either encapsulated or non-encapsulated.

[0044] In the case where the particles are encapsulated, the encapsulating material may comprise organic materials or inorganic materials such as siloxanes, silanes or derivatives thereof. By "encapsulated" we mean particles which may be coated with, or formed within a pre-defined cavity of, a macromolecular material. The encapsulating material may be a continuous unitary structure, for example a multimeric protein comprising several polypeptide chains. Alternatively, the encapsulating material may exist as

separate unitary structures which encase, at least partially, an inorganic material and either remain as juxtaposed but separate structures or interact with neighbouring structures to form a multi-component structure.

[0045] The encapsulating material may comprise a single component or a number of components that act together to accommodate a core magnetic nanoparticle which preferably has a diameter (or largest diameter in the case of non-spheroidal particles) not greater than about 100nm. Preferably the diameter is not greater than about 50nm, more preferably it is about 20nm or less. This dimension is determined, at least in part by the size of the encapsulating material. Alternatively, the encapsulating material may include a suitable opening which is not fully surrounded, but which nevertheless is capable of receiving and supporting the magnetic particle; for example, the opening may be that defined by an annulus in the macromolecule.

[0046] In aspects of the invention relating to the formation of magnetisable films and magnetic recording devices, the core magnetisable nanoparticles should not be so small that they will be incapable of maintaining ferromagnetic properties at ambient temperatures. Ambient temperatures are typically greater than about 0°C, for example greater than about 15°C. Ambient temperatures are typically less than about 50°C, for example less than about 30°C. This means that for operation at ambient temperatures, the magnetisable nanoparticles will typically be larger than 2nm.

[0047] In a preferred embodiment, the encapsulating material may be an organic macromolecule by which we mean a molecule, or assembly of molecules, and may have a molecular weight of up about 1500kD, typically less than about 500kD. Such organic macromolecular molecules may be surfactants, polymers or proteins.

[0048] Where the present invention relates to a method of forming a magnetisable film or a film of inorganic nanoparticles on a substrate, the particles are formed at least partially within an encapsulating protein shell but may be either encapsulated or non-encapsulsated when deposited onto the substrate. Where the inorganic nanoparticles are semiconductor nanoparticles, it is preferred in some aspects of the invention that these particles are deposited onto the substrate in a non-encapsulated state since this will result in a semiconductor film having a higher packing density.

[0049] Where the various aspects of the present invention involve a protein, the protein may be derived from a natural or other source, including artificial proteins, for example a recombinant protein.

[0050] In some preferred embodiments of the first, second and third aspects of the present invention, the protein serves as an encapsulating material which at least partially surrounds an inorganic particle. In a preferred embodiment the inorganic particle comprises a magnetic metal or metal alloy, or a semiconductor material.

[0051] In an embodiment of the fifth aspect of the present invention the protein is not associated, at least during the formation of a film on a substrate, with other materials.

[0052] Proteins suitable for use in the present inventions include flagellar L-P rings, bacteriophages, chaperoninins such as the bacterial GroEL and GroES, DPS and virus capsids. For example, DPS, is a ferritin homologue, dodecamer DNA protection protein comprising a hollow core and pores in the three-fold axis. Flagellar LP rings are ring-shaped structures having an inner diameter of approximately 13nm and outer diameter of approximately 20nm. They can be induced to pack into well-ordered arrays extending over several microns, approximately 13 nm thick. At more dilute concentrations, dimers can form that are approximately 26 nm thick.

[0053] In highly preferred embodiments of the present invention involving proteins, the protein is a member of the ferritin family. The present invention most preferably makes use of the iron storage protein, ferritin, whose internal cavity is used to produce nanoscale inorganic particles. Ferritin has a molecular weight of 450kD. Ferritin is utilised in iron metabolism throughout living species and its structure is highly conserved among them. It consists of 24 subunits which self-assemble to provide a hollow shell roughly 12nm in outer diameter. It has an 8nm diameter cavity which normally stores about 4500 iron(III) atoms in the form of paramagnetic ferrihydrite. This ferrihydrite can be removed (a ferritin devoid of ferrihydrite is termed "apoferritin") and other materials may be incorporated. The subunits in ferritin pack tightly; however there are channels into the cavity at the 3-fold and 4-fold axes.

[0054] A preferred protein for use in the various aspects of the invention that involve a protein is apoferritin which has a cavity of the order of 8nm in diameter.

[0055] Ferritin can be found naturally in vertebrates, invertebrates, plants, fungi, yeasts, bacteria. It can also be produced synthetically through recombinant techniques. Such synthetic forms may be identical to the natural forms, although it is also possible to synthesise mutant forms which will still retain the essential characteristic of being able to accommodate a particle within their internal cavity. The use of all such natural and synthetic forms of ferritin is contemplated within the present invention.

[0056] Ferritin may be converted to apoferritin by dialysis against a buffered sodium acetate solution under a nitrogen flow. Reductive chelation using, for example, thioglycolic acid may be used to remove the ferrihydrite core. This may be followed by repeated dialysis against a sodium chloride solution to completely remove the reduced ferrihydrite core from solution. Apoferritin has a cavity of about 8nm in the relaxed state. The core nanoparticle (that is to say the core material excluding the encapsulating material) may have a diameter up to about 15nm in diameter, as the protein can stretch to accommodate a larger particle than one 8nm in diameter.

[0057] Where, in its various aspects the present invention concerns the formation of thin films of magnetic nanoparticles the magnetic nanoparticles, which may be either encapsulated or non-encapsulated, include either ferri- or ferro-magnetic metals such as cobalt, iron, or nickel; a metal alloy, rare earth and transition metal alloy, M-type or spinel ferrite. The metal or metal alloy may contain one or more of the following: aluminium, barium, bismuth, cerium, chromium, cobalt, copper, dysprosium, erbium, europium, gadolinium, holmium, iron, lanthanum, lutetium, manganese, molybdenum, neodymium, nickel, niobium, palladium, platinum, praseodymium, promethium, samarium, strontium, terbium, thulium, titanium, vanadium, ytterbium, and yttrium or any mixture thereof.

[0058] Preferably said magnetic nanoparticles comprise a binary alloy or ternary alloy such as cobalt-nickel, iron-platinum, cobalt-palladium, iron-palladium, samarium-cobalt, dysprosium-iron-turbide or neodymium-iron boride, iron-cobalt-platinum, cobalt-nickel platinum, or cobalt-nickel-chromium. More preferably, said nanoparticles comprise cobalt or platinum or alloys thereof, e.g. an alloy of cobalt and platinum.

[0059] In a preferred embodiment of the first aspect of the invention, the magnetic nanoparticles are encapsulated by a protein material.

[0060] In a preferred embodiment of the third aspect of the invention, the particles are either magnetic nanoparticles or semiconductor nanoparticles encapsulated by a protein material. In a specific embodiment of this aspect of the invention the magnetic particles comprise either an alloy of cobalt/platinum or iron/platinum which are encapsulated by apoferritin or DPS.

[0061] The magnetic nanoparticles may be prepared by a process in which a suspension of the encapsulating material such as an organic macromolecule, typically in an aqueous medium, is combined with a source of ions of the appropriate metal or metals to comprise or consist the core magnetic nanoparticle. In this process, it is preferred that the source of metal ions be added incrementally to the source of the encapsulating material. For example the cation and anion sources may be added in sufficient amounts to provide more than 1 atom of the cation and anion sources per encapsulating shell per iteration, preferably more than 20 atoms of the cation and anion sources per encapsulating shell per iteration. The cation and anion sources may be added in sufficient amounts to provide fewer than 200 atoms of the cation and anion sources per encapsulating shell per iteration, preferably fewer than 100 atoms of the cation and anion sources per encapsulating shell per iteration. Preferably, the cation and anion sources may be added in sufficient amounts to provide about 50 atoms of the cation and anion sources per encapsulating shell per iteration. These low concentrations may be achieved by successive dilutions of solutions containing the cation and anion sources. The source of metal ions may be a salt of the metal or metals, for example tetrachloroammoniumplatinate, comprising a magnetic nanoparticle. Alternatively, but presently less preferred, the source of metal ions may be present in a composition to which a source of organic macromolecule is added.

[0062] The mixture of organic macromolecules and metal ions may be agitated to ensure homogenisation. Where the magnetic nanoparticle is to comprise an elemental metal or alloy, a reduction is effected on the composition whereby a nanoscale metal particle forms within the organic macromolecule cavity. This reduction preferably takes place under an inert atmosphere to protect the metal nanoparticles from oxidation, which would reduce their magnetic properties. The reduction/oxidation step may be repeated between additions of metal ions (which may be the same or different in each cycle) to build up the nanoparticles.

[0063] The reaction mixture may be formed at a temperature below the preferred temperature at which the magnetic nanoparticles are allowed to form and then raised to that temperature. Alternatively, the source of encapsulating material to which the source(s) of metal ions is to be added may be held at a temperature of at least 24°C and the metal ion source(s) added thereto.

[0064] Proteins can generally withstand temperatures of up to 70°C before they lose their tertiary structure. Thus in embodiments wherein the encapsulating material is a protein, the temperature of the reaction may range up to about 70°C. For these embodiments, the reaction temperature is preferably maintained above 25°C, for example above about 35°C. The temperature is preferably maintained below about 60°C, for example below about 50°C.

[0065] During the formation of encapsulated magnetic nanoparticles for use in the present invention, the aqueous medium is maintained at alkaline pH during the formation of the magnetic core nanoparticles within the macromolecular templates. The pH is preferably maintained in the range from 7.5-8.5. This may be achieved by the use of a buffer solution. Suitable solutions will vary depending on the encapsulating agent used.

[0066] Following preparation of the nanoparticles, they are placed into a carrier fluid prior to deposition onto the substrate surface. If the nanoparticles are prepared in a suspension, the suspension may form a component or the entirety of the carrier fluid. Alternatively, the nanoparticles may be extracted from the suspension in which they have been prepared and re-suspended in the carrier fluid. The physical properties of this fluid may be adjusted depending on the application. For example in the case of protein-encapsulated nanoparticles, the ambient conditions, for example temperature, pH and ionic strength, may be maintained at levels suitable to avoid unnecessary damage to the protein prior to deposition.

[0067] The properties of the carrier fluid may also be modified in order to provide easy deposition of fluid droplets onto the substrate surface. For example, the surface tension of the carrier fluid may be modified to give improved spreadability. The carrier fluid may be aqueous or non-aqueous and may have additional additives to modify its physical properties. In a preferred embodiment, the carrier fluid is water.

[0068] Where, in one embodiment, the present invention concerns the deposition of inorganic nanoparticles encapsulated by a macromolecular material by ink-jet printing, the inorganic nanoparticle is preferably a semiconductor particle.

[0069] In a highly preferred embodiment of the third aspect of the invention there is provided a method of forming a film of semiconductor nanoparticles wherein said particles comprise either CdS, CdSe, CdTe, ZnS, ZnSe, or ZnTe which are encapsulated by apoferritin or DPS.

[0070] In some embodiments of either the first, second or third aspects of the invention after the nanoparticles have been deposited on a substrate, the encapsulating shell may be removed to leave the inorganic particle without a coating.

[0071] In other embodiments of the invention, the encapsulating material may be treated to leave a residue surrounding the core nanoparticle, for example the macromolecular shell may be carbonised by subjecting the substrate to an elevated temperature, for example of the order of 300 °C. Alternatively, laser pyrolysis may be used if it is desired to carbonise the nanoparticles *in situ*. The organic macromolecular shell may be burnt off by pyrolysing the nanoparticulate film at high temperatures, for example greater than about 500^{o}C. This is preferably done by controlling the inertness of the atmosphere, for example by introducing hydrogen or nitrogen into a pyrolysis vessel.

[0072] Other methods may also be employed to remove protein encapsulating material, for example enzymatic degradation or pH denaturation. In particular, the protein may be digested using proteases or denatured by adjusting the pH of the composition to a value outside the range at which the protein is stable, for example below about pH 4.0 or above about pH 9.0. The denatured protein material may then be removed by, for example, washing the substrate or exposing it to a gaseous stream. In a preferred embodiment, the protein is denatured by adjusting the pH of the composition to below about 4.0.

[0073] The formation of smooth films of nanoparticles by ink-jet printing may be enhanced by pre-treatment of the liquid suspension of particles to increase the monodispersity of the particles. Moreover, the pre-treatment may enhance film formation by removing undesirable debris. By "monodispersity" we mean the degree to which the size of the individual magnetic nanoparticles varies within a composition of the invention is low. This variation, measured in terms of the largest nano-sized dimension, should

normally be less than about 20 %, preferably less than about 10% and most preferably less than about 5%. For compositions in which the average size is relatively large, e.g. about 50nm, it is preferred that the variation is at the lower end of the above ranges, whilst for relatively small particles, e.g. about 10nm, the variation may be at the upper end of the above ranges. The sizes of the particles in accordance with the present invention can be measured using for example Transmission electron microscopy (TEM). In aspects of the invention in which the core nanoparticles are encapsulated by a macromolecular or protein shell, it may be necessary to remove the shell in a representative sample of the encapsulated nanoparticles prior to measurement of core nanoparticle size. This may be done using any method known to those skilled in the art for example by any of the methods detailed above such as pyrolysis.

[0074] We have found that monodispersity of encapsulated nanoparticles may be promoted by subjecting a liquid composition comprising the said nanoparticles to a microporous membrane filtration step prior to deposition, for example by ink jet printing, on the substrate. Moreover, this preparative step often assists in the removal of unwanted debris.

[0075] In a preparative filtration step, a composition of the encapsulated nanoparticles, preferably aqueous although other solvents such as alcohols or alkanes may be used in some embodiments, is subjected to the microporous membrane filtration step. In this filtration step, the composition is introduced to one side of the filter and filtered through the membrane. Nanoparticles for use in the present invention are preferably present in the composition in a concentration in the range from about 0.1 to about 20mg/ml. In an embodiment, the pH of the composition is preferably in the range from about 7 to about 8.5. Preferably, the composition is subjected to an applied positive pressure during the filtration step. For example the applied pressure may be greater than about 1psi, for instance greater than about 5psi. Normally, the pressure will be less than about 20 psi, for instance less than about 15 psi. The filtrate, which comprises a composition of the nanoparticles is then recovered.

[0076] Membrane filters are well known structures which are distinguished from non-membrane filters by the fact that membranes have a structure which is monolithic, i.e. the solid structure is permanently bonded forming a continuous solid phase. In contrast, non-

membrane filters are formed by fibres held in place by mechanical entanglement or other surface forces. Membrane filters can be made with a narrow pore size distribution and very small pores when necessary. The microporous membranes used in the present invention have pores approximately in the range from about 0.02 to about 10μm, preferably less than about 1μm and most preferably less than about 0.5μm; specific examples of pore sizes which may be used in the present invention are pores of about 0.2μm and pores of about 0.1μm. The microporous filter for fractionating particles to be used in the present invention may be made from various materials, including polymers, metals, ceramics, glass and carbon. Typically the membrane will be formed of a polymeric material known in the art to be used in membrane filtration, such as for example polysulphones, polyethersulphones (PES), polyacrylates, polyvinylidenes, for example polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), cellulose, cellulose esters or co-polymers thereof. Preferably where the encapsulating material is a protein, the membrane will be selected to comprise a low protein-binding material such as a polyethersulphone or a polyvinylidene. Such microporous filters are available from Millipore Corporation (Bedford, MA).

[0077] The membrane filter may be a membrane disk, although other forms of membrane filters are usable in the present invention.

[0078] Significantly, we have found that to achieve the production of stable nanoparticles compositions filter pore size can be several orders of magnitude greater than that of the nanoparticulate material. For example, where particles for use in the present invention are encapsulated by ferritin this protein has an approximate diameter of 12nm. We have found that stable preparations of ferritin-encapsulated nanoparticles which are resistant to aggregation can be achieved using 0.2μm and 0.1μm filters.

[0079] Normally, the nanoparticles to be used in the present invention will have all of their dimensions in the nano size range, typically at least about 1nm and no greater than about 100nm, preferably no greater than about 50nm and more preferably no greater than about 20nm. Preferably magnetic or semiconductor nanoparticles of the invention are substantially spheroidal having a diameter in the range from about 1-100nm. However, the present invention also extends to magnetic particles which have one dimension which is not within the nanosize range.

[0080] Where the present invention involves magnetic nanoparticles, pre-treatment purification steps may include a magnetic fractionation step of encapsulated magnetic nanoparticles. This involves passing a liquid composition comprising the magnetic nanoparticles through a retarding medium under gravity or by the exertion of a positive pressure whilst subjecting it to a magnetic field, such that the particles within the composition are spatially separated according to their magnetic properties. Since the magnetic properties of the magnetic nanoparticles, whether encapsulated or not, will be determined by the size of the core magnetic nanoparticle, this method also provides a means for obtaining a composition wherein the core particles have a high degree of monodispersity.

[0081] The retarding medium may comprise steel, for example type IV 20L, or another suitable soft-magnetic material in the form of a powder, beads or other form known in the art. It is preferred that the retarding medium comprise a material which does not react chemically with the magnetic nanoparticle composition in such a way as to damage or alter its structure, although it may be such that the magnetic nanoparticles have some form of attractive interaction during their passage through the fractionating device.

[0082] One skilled in the art would appreciate that many means for magnetic fractionation are available such as magnetic wire, magnetic powder chromatography and field-flow fractionation techniques. In a preferred embodiment of the invention, the composition is passed through columns comprising magnetic powder at flow rates ranging from about 0.2-10ml/min^{-1}. Magnetic fractionation also provides the advantage of enabling the fluid medium in which the nanoparticles are suspended to be exchanged.

[0083] Where the particles are magnetic particles, a pre-treatment phase may include either a filtration step or magnetic fractionation step or both steps in any sequence.

[0084] The invention is now illustrated by reference to the following non-limiting examples:

[0085] Examples

[0086] Apoferritin was produced as described in WO 98/22942.

[0087] **Example 1. Synthesis of cobalt/platinum nanoparticles within apoferritins**

[0088] Apoferritin was dispersed in either 0.05M 4-(2-hydroxyethyl)-1-piperazineethane-sulfonic acid (HEPES) buffer, buffered to pH 7.5-8.5 or 0.25M AMPSO buffered to pH7-5.8.5. Aliquots of 0.1M cobalt (II) acetate solution and 0.1M ammonium tetrachloroplatinate (II) solution were then added and the mixture stirred at a temperature between 35 ^{o}C and 50^{o}C. This was followed by reduction using sodium borohydride. A number of metal salt additions and subsequent reductions were performed to obtain apoferritin in which the cores were substantially occupied by Co/Pt crystals (*Mayes E 2002. J. Magn. Soc. Japan. 26 (8) 932-935: Warne B et.al. 2000 IEE Transactions on Magnetics 36 3009-3011*).

[0089] **Example 2. Synthesis of iron-platinum nanoparticles within apoferritins**

[0090] Apoferritin was dispersed in 50mM 3-([1,1-dimethyl-2-hydroxyethyl]amino)-2-hydroxypropane sulphonic acid (AMPSO) solution and buffered to between pH 8.5 and 8.9; the suspension temperature being maintained at between 40 ^{o}C and 70°C. Aliquots from deaerated solutions of ammonium iron (II) sulphate (25mM) and ammonium tetrachloroplatinate (II) (25mM) were added incrementally to the apoferritin suspension. The aliquots of iron (II) and platinum (II) added was equivalent to 100 atoms per apoferritin molecule. Following each addition of iron (II), a stoichiometric aliquot, equivalent to 2/3 of iron (II), of trimethylamine-N-oxide (25mM) was added. After each addition of platinum (II), a suitable reductant, for example sodium borohydride or hydrazine, was added in a stoichiometric amount. The increment interval for the addition of aliquots was approximately 15 minutes, except for the addition of the iron (II) oxidant which was performed immediately following the addition of iron (II) to the reaction suspension. Additions were made until the apoferritin cores were substantially occupied by magnetite/platinum (0) cores. The suspension was then dialysed against water and filtered through 0.2um filter before concentrating or using as prepared.

[0091] Example 3. Ink-jet printing ferritin onto glass substrates

[0092] Glass substrates were cleaned using an Oliver Design (SN252) multiple cassette disk cleaning system.

[0093] An EPSON ink-jet printer (photo1290) was used in the following procedure: aqueous suspensions of ferritin having a protein concentration of approximately 2-10 mg/ml were introduced into the head of the printer which has a static head of -5cm (approx. 0.075psi) using a syringe.

[0094] Disks were loaded into the disk holding cassette and arranged in a stationary position beneath the ink-jet head. Ferritin suspensions were deposited on the glass disks at varying head speeds ranging between 10 and 100cm sec^{-1}.

[0095] In some cases the disks were subject to another round of ink-jet printing using the same ferritin material.

[0096] After deposition of the ferritin the disks were removed and analysed by Atomic Force Microscopy. It was found that this application process yielded films having thicknesses ranging between 100nm and 12nm, the latter being characteristic of a ferritin monolayer. A sample AFM micrograph is shown in Figure 5.

[0097] Example 4. Ink-jet printing apoferritin-encapsulated cobalt-platinum onto glass substrates

[0098] Glass substrates were cleaned using an Oliver Design (SN252) multiple cassette disk cleaning system.

[0099] An EPSON ink-jet printer (photo1290) was used in the following procedure: aqueous suspensions (which may contain up to 0.2% hydrazine) of apoferritin-encapsulated cobalt/platinum alloy as per Example 1 having a protein concentration of approximately 2-10 mg/ml were introduced into the head of the printer which has a static head of -5cm (approx. 0.075psi) using a syringe.

[00100] Disks were loaded into the disk holding cassette and arranged in a stationary phase beneath the ink-jet head. Compositions of the apoferritin-encapsulated metal alloys were deposited on the glass disks at varying head speeds ranging between 10 and 100cm sec^{-1}.

[00101] In some cases the disks were subject to another round of ink-jet printing using the same apoferritin-encapsulated cobalt-platinum material.

[00102] Example 5. Ink-jet printing ferritin onto glass substrates pretreated with UV-light

[00103] Glass substrates were cleaned using an Oliver Design (SN252) multiple cassette disk cleaning system.

[00104] Substrates were exposed to a UV light source (wavelength 172 nm) (USHIO) under a nitrogen atmosphere prior to the ink-jet printing. Specifically, substrates were positioned approximately 2mm from quartz glass encasing the UV filaments and exposed to UV light for approximately 20 to 40 seconds.

[00105] An EPSON ink-jet printer (photo1290) was used in the following procedure: aqueous suspensions (which may contain up to 0.2% hydrazine) of ferritin having a protein concentration of approximately 2-10 mg/ml were introduced into the head of the printer which has a static head of -5cm (approx. 0.075psi) using a syringe.

[00106] Disks were loaded into the disk holding cassette and arranged in a stationary phase beneath the ink-jet head. Compositions of the ferritin were deposited on the glass disks at varying head speeds ranging between 10 and 100cm sec^{-1}.

[00107] In some cases, the disks were subject to another round of ink-jet printing using the same batch of ferritin.

[00108] AFM micrographs of a non-irradiated and a UV-irradiated sample are shown in Figure 6.

[00109] **Example 6. Ink-jet printing apoferritin-encapsulated iron-platinum onto glass substrates pretreated with UV-light**

[00110] Glass substrates were cleaned using an Oliver Design (SN252) multiple cassette disk cleaning system.

[00111] Substrates were exposed to a UV light source (wavelength 172 nm) (USHIO) under a nitrogen atmosphere prior to the ink-jet printing. Specifically, substrates were positioned approximately 2mm from quartz glass encasing the UV filaments and exposed to UV light for approximately 20 to 40 seconds.

[00112] An EPSON ink-jet printer (photo1290) was used in the following procedure: aqueous suspensions (which may contain up to 0.2% hydrazine) of apoferritin-encapsulated iron/platinum alloy as per Example 2 having a protein concentration of

approximately 2-10 mg/ml were introduced into the head of the printer which has a static head of -5cm (approx. 0.075psi) using a syringe.

[00113] Disks were loaded into the disk holding cassette and arranged in a stationary phase beneath the ink-jet head. Compositions of the apoferritin-encapsulated metal alloys were deposited on the glass disks at varying head speeds ranging between 10 and 100cm sec^{-1}.

[00114] In some cases the disks were subject to another round of ink-jet printing using the same apoferritin-encapsulated cobalt-platinum material.

[00115] **Example 7 Ink-jet printing apoferritin-encapsulated cobalt-platinum onto glass substrates pretreated with UV-light**

[00116] Glass substrates were cleaned using an Oliver Design (SN252) multiple cassette disk cleaning system.

[00117] Substrates were exposed to a UV light source (wavelength 172 nm) (USHIO) under a nitrogen atmosphere prior to the ink-jet printing. Specifically, substrates were positioned approximately 2mm from quartz glass encasing the UV filaments and exposed to UV light for approximately 20 to 40 seconds.

[00118] An EPSON ink-jet printer (photo1290) was used in the following procedure: aqueous suspensions (which may contain up to 0.2% hydrazine) of apoferritin-encapsulated cobalt/platinum alloy as per Example 1 having a protein concentration of approximately 2-10 mg/ml were introduced into the head of the printer which has a static head of -5cm (approx. 0.075psi) using a syringe.

[00119] Disks were loaded into the disk holding cassette and arranged in a stationary phase beneath the ink-jet head. Compositions of the apoferritin-encapsulated metal alloys were deposited on the glass disks at varying head speeds ranging between 10 and 100cm sec^{-1}.

[00120] In some cases the disks were subject to another round of ink-jet printing using the same apoferritin-encapsulated cobalt-platinum material.

CLAIMS

1. A method of forming a magnetic recording device having a film of magnetisable nanoparticles, which comprises preparing a suspension of magnetisable nanoparticles in a carrier fluid and depositing the said fluid suspension onto a substrate surface as droplets having a volume less than about 1nl to form said film of magnetisable nanoparticles as a dry residue of the deposited fluid suspension.

2. A method in accordance with claim 1, wherein said fluid suspension is deposited onto the substrate using ink jet printing.

3. A method in accordance with claim 1 or claim 2, wherein said magnetic nanoparticles have been formed at least partially within a macromolecular shell.

4. A method in accordance with claim 3, wherein said macromolecular shell is a protein.

5. A method in accordance with claim 4, wherein said protein is apoferritin or DPS

6. A method in accordance with any of claims 3 to 5, wherein said macromolecular shell is subsequently carbonised by subjecting the nanoparticulate film to an elevated temperature above 300°C.

7. A method in accordance with any of claims 3 to 5, wherein said macromolecular shell is subsequently burnt off by pyrolising the nanoparticulate film at a temperature of greater than 500°C.

8. A method in accordance with any preceding claim, wherein the average surface roughness, R_a, of the substrate is less than about 1nm.

9. A method in accordance with any of claims 1 to 7, wherein the average surface roughness, R_a, of the substrate is in the range from about 5nm to about 20nm.

10. A method in accordance with any preceding claim, wherein the substrate is treated to promote the dispersion of the applied suspension of nanoparticles.

11. A method in accordance with claim 10, wherein the treatment comprises chemical, mechanical or radiation treatment.

12. A method in accordance with claim 11, wherein the radiation treatment comprises exposure of the substrate to UV light.

13. A method in accordance with any preceding claim, wherein the film is treated following deposition of the nanoparticles onto the substrate.

14. A method in accordance with claims 13, wherein the film is annealed after deposition of the nanoparticles onto the substrate.

15. A method in accordance with any preceding claim, wherein the film thickness is no greater than 2 particle diameters (including any encapsulating shell) substantially throughout the film.

16. A method in accordance with any preceding claim, wherein discontinuities in the film surface are less than about 13nm in height.

17. A method in accordance with any preceding claim, wherein the magnetic nanoparticles have a diameter (or largest diameter in the case of non-spheroidal particles) of 20nm or less.

18. A method in accordance with any preceding claim wherein the magnetic nanoparticles comprise an alloy of cobalt and platinum.

19. A method in accordance with any preceding claim, wherein the magnetic nanoparticles are encapsulated.

20. A method in accordance with claim 19, wherein the encapsulating material is a protein.

21. A method in accordance with claim 20, wherein said protein is apoferritin or DPS.

22. A method in accordance with any one of claims 19 to 21, wherein the composition of encapsulated nanoparticles is subjected to a microporous membrane filtration step prior to deposition onto the substrate.

23. A method in accordance with claim 22, wherein the pore size of said membrane filter is in the range from 0.02-10μm.

24. A method in accordance with claims 22 or 23, wherein said membrane comprises polyethersulphone or a polyvinylidene.

25. A method in accordance with any preceding claim, wherein the magnetic nanoparticles are subjected to a magnetic fractionation step prior to deposition onto the substrate.

26. A method of forming a magnetisable film, which comprises preparing a suspension of magnetisable nanoparticles, each having been formed at least partially within a protein

shell, in a carrier fluid and depositing the said fluid suspension onto a substrate surface as droplets having a volume less than about 1nl to obtain said magnetisable film on the substrate as a dry residue of the deposited fluid suspension.

27. A method in accordance with claim 26, wherein the fluid suspension is deposited onto the substrate using ink jet printing.

28. A method in accordance with claim 26 or claim 27, wherein said protein shell is subsequently carbonised by subjecting the nanoparticulate film to an elevated temperature above 300°C.

29. A method in accordance with claim 26 or claim 27, wherein said protein shell is subsequently burnt off by pyrolising the nanoparticulate film at a temperature of greater than 500°C.

30. A method in accordance with any of claims 26 to 29, wherein the average surface roughness, R_a, of the substrate is less than about 1nm.

31. A method in accordance with any of claims 26 to 29, wherein the average surface roughness, R_a, of the substrate is in the range from about 5nm to about 20nm.

32. A method in accordance with any of claims 26 to 31, wherein the substrate is treated to promote the dispersion of the applied suspension of nanoparticles.

33. A method in accordance with claim 32, wherein the treatment comprises chemical, mechanical or radiation treatment.

34. A method in accordance with claim 33, wherein the radiation treatment comprises exposure of the substrate to UV light.

35. A method in accordance with any of claims 26 to 34, wherein the film is treated following deposition of the nanoparticles onto the substrate.

36. A method in accordance with claims 35, wherein the film is annealed after deposition of the nanoparticles onto the substrate.

37. A method in accordance with any of claims 26 to 36, wherein the film thickness does not vary by more than about three diameters of the constituent particles (including any encapsulating shell) substantially throughout the film.

38. A method in accordance with any of claims 26 to 37, wherein the average surface roughness, R_a, of the film is not greater than about 3 particle diameters (including any encapsulating shell).

39. A method in accordance with any of claims 26-38, wherein the composition of encapsulated nanoparticles is subjected to a microporous membrane filtration step prior to deposition onto the substrate.

40. A method in accordance with any of claims 26 to 39, wherein the magnetic nanoparticles have a diameter (or largest diameter in the case of non-spheroidal particles) of 20nm or less.

41. A method in accordance with any of claims 26 to 40, wherein the magnetic nanoparticles comprise an alloy of cobalt and platinum.

42. A method in accordance with any of claims 26 to 41, wherein the encapsulating material is a protein.

43. A method in accordance with claim 42, wherein said protein is apoferritin or DPS.

44. A method in accordance with any of claims 26 to 43, wherein the composition of encapsulated nanoparticles is subjected to a microporous membrane filtration step prior to deposition onto the substrate.

45. A method in accordance with claim 44, wherein the pore size of said membrane filter is in the range from 0.02-10μm.

46. A method in accordance with claims 44 or 45, wherein said membrane comprises polyethersulphone or a polyvinylidene.

47. A method in accordance with any of claims 26 to 46, wherein the magnetic nanoparticles are subjected to a magnetic fractionation step prior to deposition onto the substrate.

48. A method of forming a film of inorganic nanoparticles on a substrate, which comprises preparing a suspension of inorganic nanoparticles, each having been formed at least partially within a protein shell, in a carrier fluid and depositing the said fluid suspension onto a substrate surface as droplets having a volume less than about 1nl to obtain said film on the substrate as a dry residue of the deposited fluid suspension.

49. A method in accordance with claim 48, wherein said fluid suspension is deposited onto the substrate using ink jet printing.

50. A method in accordance with claim 48 or claim 49, wherein said protein shell is subsequently carbonised by subjecting the substrate to an elevated temperature above 300°C.

51. A method in accordance with claim 48 or claim 49, wherein said macromolecular shell is subsequently burnt off by pyrolising the nanoparticulate film at a temperature of greater than about 500°C.

52. A method in accordance with any of claims 48 to 51, wherein the average surface roughness, R_a, of the substrate is less than about 1nm.

53. A method in accordance with any of claims 48 to 51, wherein the average surface roughness, R_a, of the substrate is in the range from about 5nm to about 20nm.

54. A method in accordance with any of claims 48 to 53, wherein the substrate is treated to promote the dispersion of the applied suspension of nanoparticles.

55. A method in accordance with claim 54, wherein the treatment comprises chemical, mechanical or radiation treatment.

56. A method in accordance with claim 55, wherein the radiation treatment comprises exposure of the substrate to UV light.

57. A method in accordance with any of claims 48 to 56, wherein the film is treated following deposition of the nanoparticles onto the substrate.

58. A method in accordance with claims 57, wherein the film is annealed after deposition of the nanoparticles onto the substrate.

59. A method in accordance with any of claims 48 to 58, wherein the film thickness does not vary in depth by more than about three diameters of the constituent particles (including any encapsulating shell).

60. A method in accordance with any of claims 48 to 59, wherein the average surface roughness, R_a, of the film is not greater than about 3 particle diameters (including any encapsulating shell).

61. A method in accordance with any of claims 48 to 60, wherein said inorganic nanoparticles comprise magnetic materials or semiconductor materials.

62. A method in accordance with claim 61, wherein said inorganic nanoparticles comprise semiconductor materials.

63. A method in accordance with claim 62, wherein said inorganic nanoparticles are semiconductor nanoparticles comprising CdS, CdSe, CdTe, ZnS, ZnSe, or ZnTe which are encapsulated by apoferritin or DPS.

64. A method in accordance with any of claims 48 to 63, wherein the composition of encapsulated nanoparticles is subjected to a microporous membrane filtration step prior to deposition onto the substrate.

65. A method in accordance with any of claims 48 to 64, wherein the magnetic nanoparticles have a diameter (or largest diameter in the case of non-spheroidal particles) of 20nm or less.

66. A method in accordance with any of claims 48 to 65, wherein said protein shell comprises apoferritin or DPS.

67. A method in accordance with any of claims 48 to 66, wherein the composition of encapsulated nanoparticles is subjected to a microporous membrane filtration step prior to deposition onto the substrate.

68. A method in accordance with claim 67, wherein the pore size of said membrane filter is in the range from 0.02-10μm.

69. A method in accordance with any of claims 67 or 68, wherein said membrane comprises polyethersulphone or a polyvinylidene.

70. A method of forming a protein thin film on the surface of a substrate, said protein thin film having a thickness of less than 10 times the diameter of its constituent protein particles substantially throughout the film, which comprises preparing a suspension of protein particles in a carrier fluid, said protein particles having been subjected to a membrane filtration step, and depositing the said fluid suspension onto a substrate surface as droplets having a volume less than about 1nl to obtain said film on the substrate as a dry residue of the deposited fluid suspension.

71. A method in accordance with claim 70, wherein said fluid suspension is deposited onto the substrate using ink jet printing.

72. A method in accordance with any of claims 70 or 71, wherein the surface roughness, R_a, of the substrate is less than about 1nm.

73. A method in accordance with claim 70 or claim 71, wherein the surface roughness, R_a, of the substrate is in the range from about 5nm to about 20nm.

74. A method in accordance with any of claims 70 to 73, wherein the substrate is treated to promote the dispersion of the applied suspension of protein particles.

75. A method in accordance with claim 74, wherein the treatment comprises chemical, mechanical or radiation treatment.

76. A method in accordance with claim 75, wherein the radiation treatment comprises exposure of the substrate to UV light.

77. A method in accordance with any of claims 70 to 76, wherein the film is treated following deposition of the protein particles onto the substrate.

78. A method in accordance with any of claims 70 to 77, wherein the film is annealed after deposition of the protein particles.

79. A method in accordance with any of claims 70 to 78, wherein the film thickness does not vary in depth by more than three diameters of the constituent protein particles substantially throughout the film.

80. A method in accordance with any of claims 70 to 79, wherein the surface roughness, R_a, of the film is not greater than about 3 particle diameters.

81. A method in accordance with any of claims 70 to 80, wherein said protein is apoferritin or DPS.

82. A method in accordance with any of claims 70 to 81, wherein the composition of protein nanoparticles is subjected to a microporous membrane filtration step prior to deposition onto the substrate.

83. A method in accordance with claim 82, wherein the pore size of said membrane filter is in the range from 0.02-10μm.

84. A method in accordance with claim 82 or claim 83, wherein said membrane comprises polyethersulphone or a polyvinylidene.

85. A magnetic recording device having a film of magnetisable nanoparticles, wherein said nanoparticles have been prepared in a suspension in a carrier fluid and deposited onto a substrate surface as droplets having a volume less than about 1 nl to form said film of magnetisable nanoparticles as a dry residue of the deposited fluid suspension.

86. The magnetic recording device of claim 85, wherein said nanoparticles are deposited onto said substrate by ink jet printing.

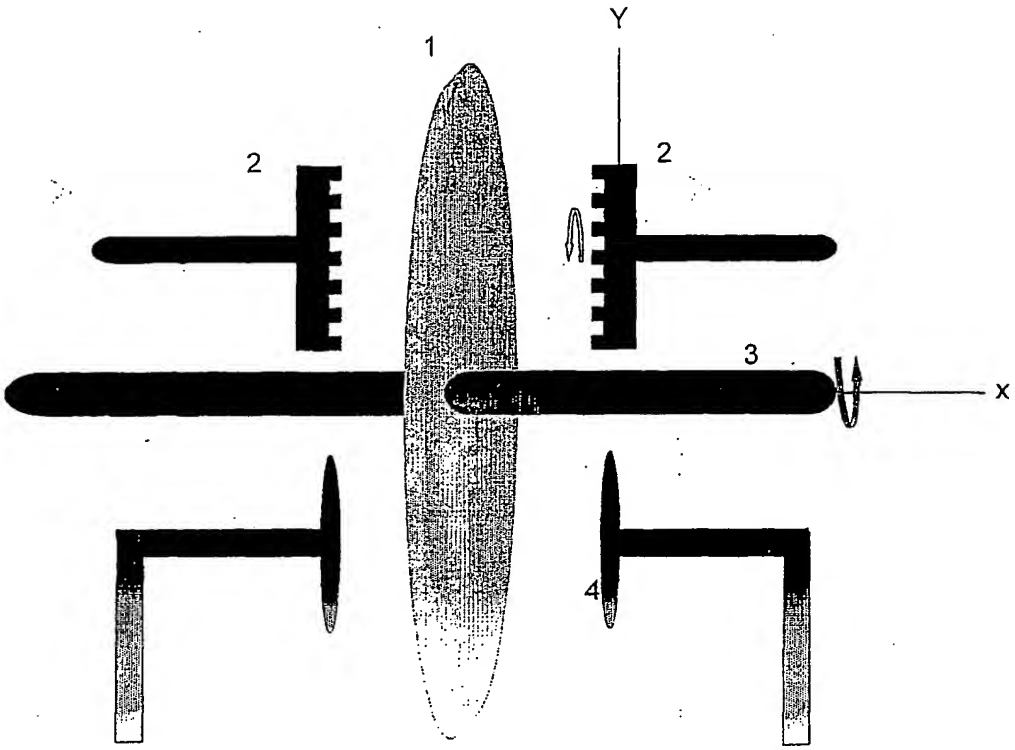


Figure 1. An ink-jet printing device wherein the substrate is arranged in a vertical position.

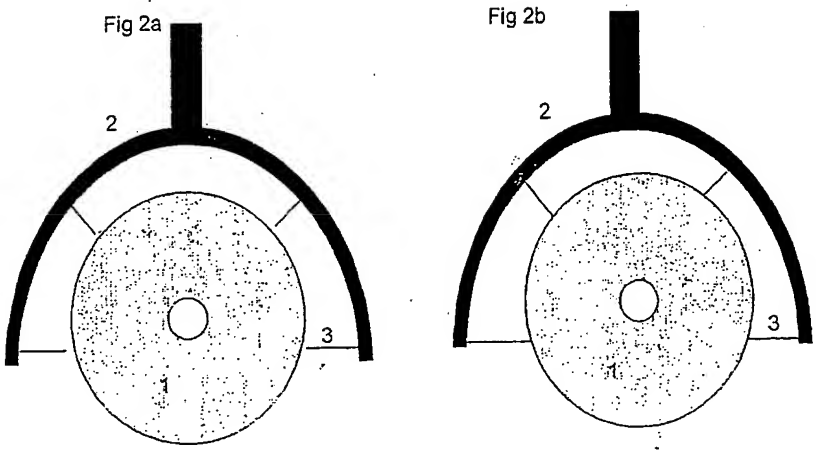


Figure 2. A substrate positioning device in a first substrate-disengaged position and second substrate-engaged position.

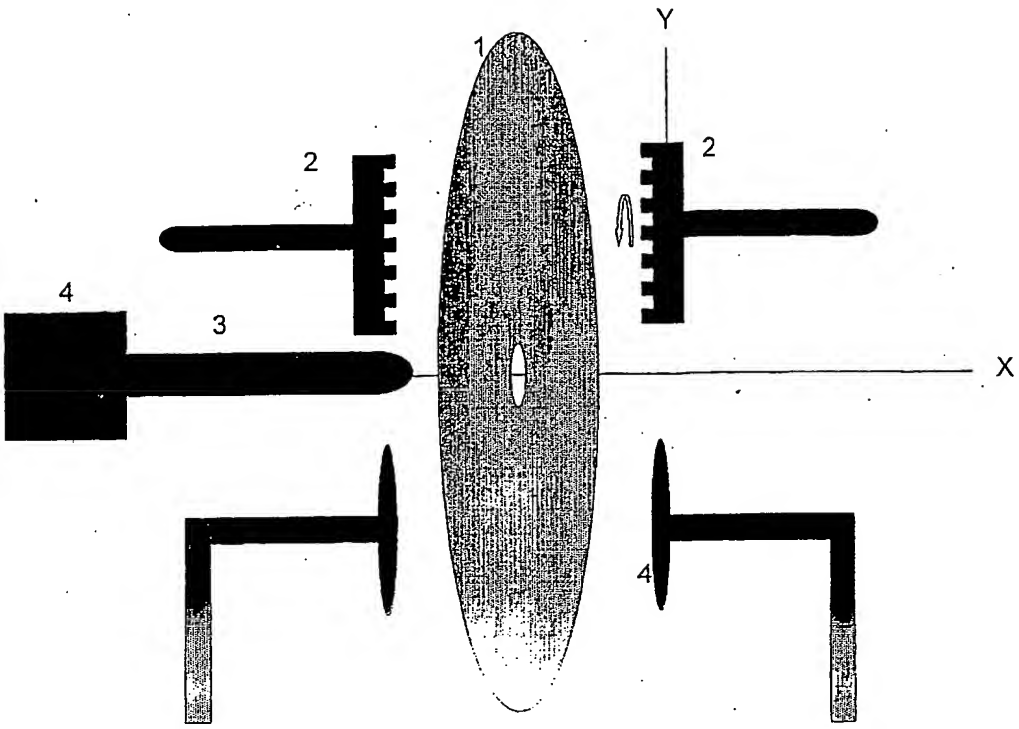


Figure 3. An ink-jet printing device wherein the spindle is in a retracted position.

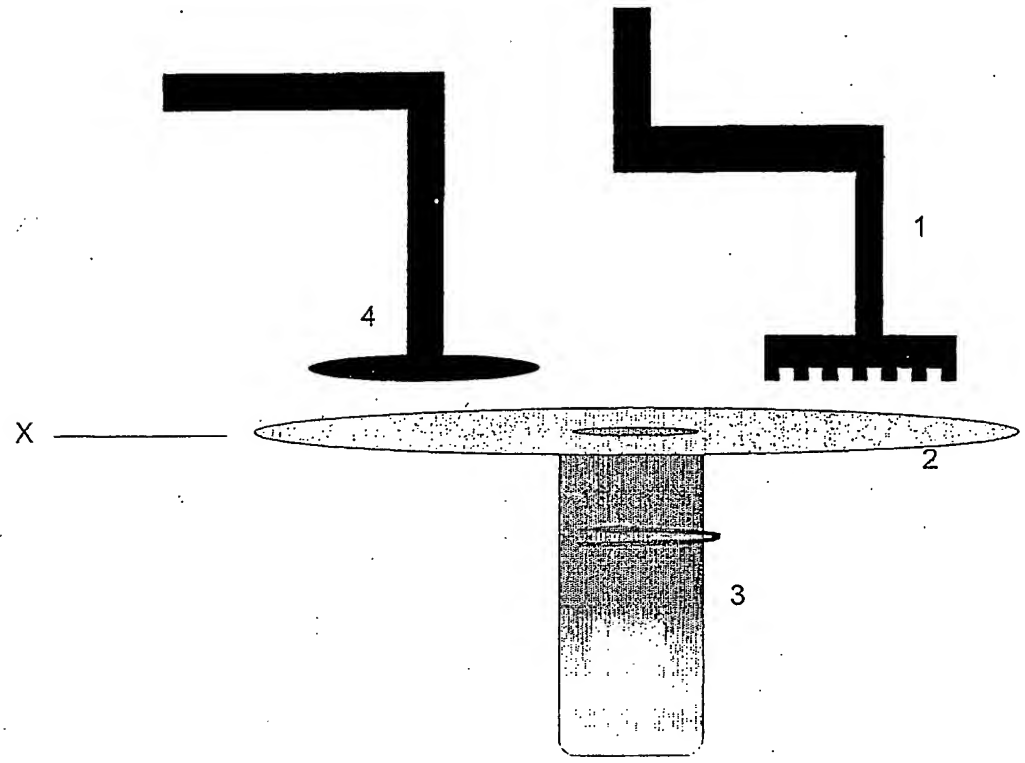


Figure 4. An ink-jet printing device wherein a substrate is arranged in a horizontal position.

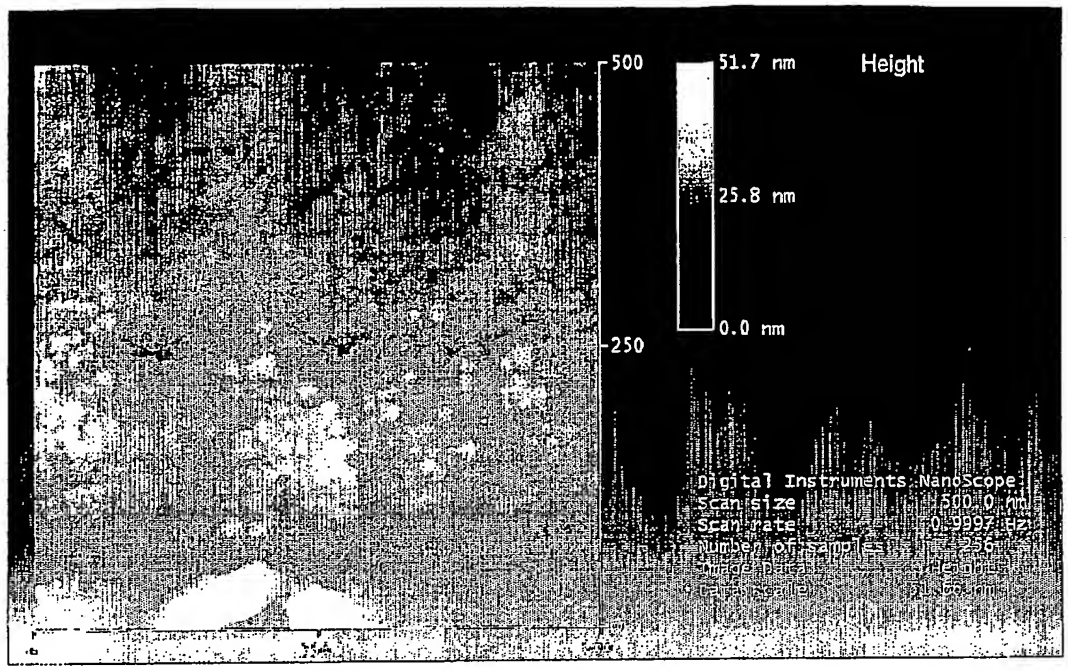
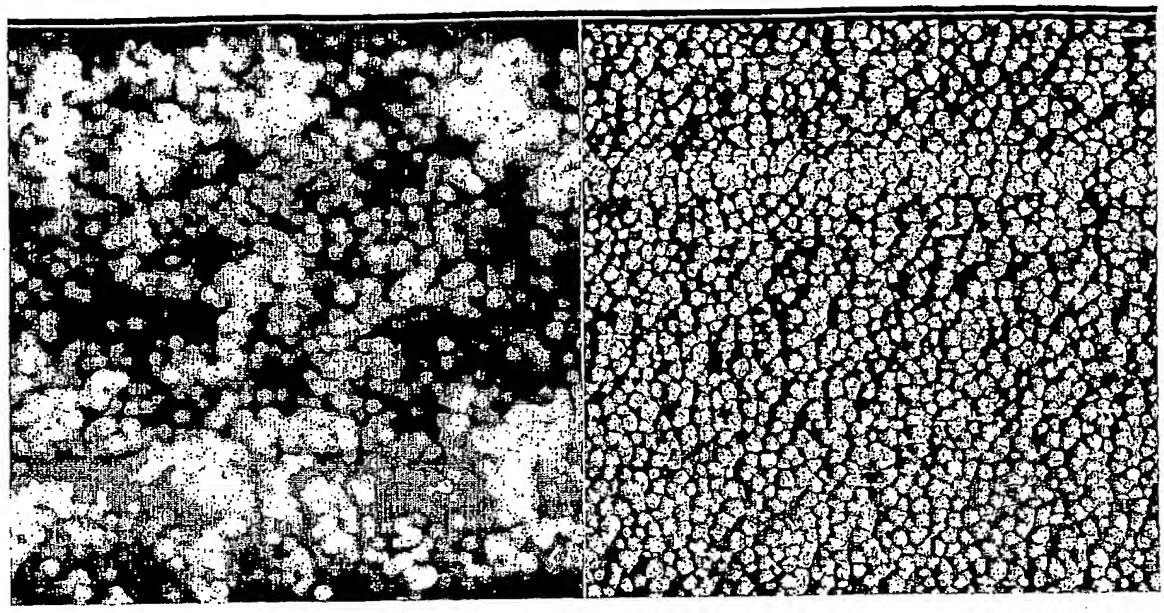


Figure 5. A tapping-mode AFM image of ferritin deposited onto a glass substrate.



500nm

Figure 6. A tapping-mode AFM image of ferritin deposited onto a glass substrate where the substrate has been pretreated with UV light.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/000999

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G11B5/842 G11B5/712 H01F41/16 H01F10/00 H01F1/00
A61K9/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G11B H01F A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PAUL CALVERT: "Inkjet Printing for Materials and Devices" CHEM. MATER., vol. 13, 9 December 2001 (2001-12-09), pages 3299-3305, XP002284900 cited in the application the whole document	1-3,6,7, 13,14, 26-29, 35,36, 48-51, 57,58, 61,70, 71,85,86
A	EP 1 217 616 A (NANOMAGNETICS LTD) 26 June 2002 (2002-06-26) claims 1,3-8 paragraphs [0001], [0009]	1,3-5, 17-21, 26, 40-43, 48,61, 65,66 85,86

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 June 2004	07.07.2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Stichauer, L

INTERNATIONAL SEARCH REPORT

PCT/GB2004/000999

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevent to claim No.
A	US 6 361 161 B1 (CARLTON DONN B ET AL) 26 March 2002 (2002-03-26) claims 1,3,6 column 1, line 46 - column 5, line 65	1,2,17, 26,27, 40,48, 49,61, 62,65, 85,86
A	WO 96/22533 A (FIRST MEDICAL INC) 25 July 1996 (1996-07-25) cited in the application claims 1,2,4,8,15-17,19,23,25 page 4, line 21 - line 25 page 8, line 34 - line 37 page 11, line 35 - page 13, line 2	1,2, 10-14, 26,27, 32-36, 48,49, 54-58, 70,71, 74-78
A	US 2003/048341 A1 (STEARNS RICHARD G ET AL) 13 March 2003 (2003-03-13) claims 1,4,15,16,42,116,124,130,136,142 paragraphs [0050], [0057], [0061], [0062], [0077], [0082], [0106] example 4	1,8-11, 26, 30-33, 48, 52-55, 61-63, 70, 72-75,85
A	US 2001/055669 A1 (GOLDWASSER ISY ET AL) 27 December 2001 (2001-12-27) claims 13,16-19,21,31-33,53,54,59,87,92-95,97,101 paragraphs [0004], [0012], [0017] - [0019], [0066], [0073], [0092], [0130] - [0136], [0176], [0177], [0225] - [0227] tables I,VI	1,2,10, 11,26, 27,32, 33,48, 49,54, 55,61, 62,70, 71,74, 75,85,86

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INTERNATIONAL SEARCH REPORT

PCT/GB2004/000999

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RODA A ET AL: "Protein microdeposition using a conventional ink-jet printer" BIOTECHNIQUES, EATON PUBLISHING, NATICK, US, vol. 28, no. 3, March 2000 (2000-03), pages 492-496, XP002164952 ISSN: 0736-6205 cited in the application the whole document -----	70-80

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-25,85-86

   a known method used to form a magnetic recording device, and magnetic recording device obtainable by said method

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2. claims: 26-47,48-69

   a method of forming a magnetisable film or a film of inorganic nanoparticles, said method characterized by using a suspension of magnetisable or inorganic nanoparticles, each having been formed within a protein shell

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3. claims: 70-84

   a method of forming a protein thin film, said method characterized by including a membrane filtration step

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2004/000999

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/GB2004/000999

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